



## Trends of Ab Initio Oxygen Reduction Reaction Energetics of $\text{LaBO}_3$ (B = Mn, Fe, Co, and Ni) for Solid Oxide Fuel Cells

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### Trends of *Ab Initio* Oxygen Reduction Reaction Energetics of LaBO<sub>3</sub> (B=Mn, Fe, Co, and Ni) for Solid Oxide Fuel Cells

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The perovskite type lanthanum strontium transition metal oxides (La,Sr)BO<sub>3</sub> (B=Mn, Fe, Co, and Ni) and closely related alloys are frequently explored as the cathode materials for solid oxide fuel cells (SOFCs) due to their ability to catalyze the oxygen reduction reaction (ORR), as well as low cost, high temperature stability and good electronic/ionic conductivity. The ORR contribution to the overpotential is expected to become increasingly important as other sources of voltage loss are reduced (*e.g.*, by the making thinner and less resistive electrolyte films) and as researchers push to lower the SOFC operating temperatures to reduce degradation rates and material costs [1]. The complex ORR mechanisms are still poorly understood, including the rate-limiting steps and how different transition metal cations alter the catalytic properties. We are using density functional theory (DFT) simulations to obtain surface oxygen binding, hopping, vacancy, and dissociation energies to understand the trends vs. transition metal types. Careful treatment of the O<sub>2</sub> gas [2] and application of the DFT+U method [3] (which corrects for the self interaction errors in the strongly correlated transition metal oxide systems) increase the accuracy of our study. Initial work is focused on the undoped LaBO<sub>3</sub> systems and {001} BO<sub>2</sub> surfaces. Surfaces are simulated with a LaBO<sub>3</sub> 8-layer slab (2×2×4 perovskite supercell) under periodic boundary conditions.

One of the issues of the DFT+U approach is the selection of U<sub>eff</sub> (defined as U-J in [4], where U is the on-site Coulomb repulsion and J is the Hund's exchange interaction). When U<sub>eff</sub> is fit to empirical data, the value can vary depending on the material properties that are fitted (band gaps, redox energetics, *etc.*). Nonetheless, it has been observed that errors in the LaBO<sub>3</sub> ORR relevant energetics can be greatly improved if an appropriate U<sub>eff</sub> is applied [5]. To understand the ORR energetic trends vs. U<sub>eff</sub> and how U<sub>eff</sub> modifies the electronic structure, we have explored a wide range of U<sub>eff</sub> (0~7 eV) for each LaBO<sub>3</sub> system. Our results suggest that adding U<sub>eff</sub> stabilizes the reduction products, or conversely, destabilize the oxidation products, which is consistent with other DFT+U studies on the redox energetics of late transition metal oxides [2, 6]. However, an anomalous inverse energetic trend vs. U<sub>eff</sub> is found in the oxygen vacancy formation reaction of bulk LaFeO<sub>3</sub>, which is due to the special half filled 3d shell configuration. Interestingly, because of partial oxidation of Fe cations in FeO<sub>2</sub> terminated (001) surfaces, the reaction energy trends with U<sub>eff</sub> for the surface oppose the bulk energetics, and thereby conform with the trends of the other LaBO<sub>3</sub> surfaces.

The ORR process at oxide surfaces is inherently complex with many possible pathways. To get directions towards new and more optimal materials, it is not only important to gain fundamental insight into the details of a

single system, but preferably to find fundamental intrinsic descriptors for the reaction process that can aid the search for new materials. Our detailed and systematic study of *ab initio* surface reaction energetics of fundamental reaction processes as oxygen adsorption, hopping, splitting and vacancy formation energies provides an excellent starting point for the search of descriptors that are likely to correlate with the ORR activity.

While tests of the commonly used *d*-band center as the descriptor for metal catalysts did not provide a clear correlation with the calculated energetics, we have observed the ORR energetics for all materials and U<sub>eff</sub> are linearly correlated with the O *p*-band center. Figure 1 shows the surface oxygen vacancy formation energies and O above surface B site adsorption energies as a function of the O *p*-band center. Each point corresponds to different B metal cations and/or different U<sub>eff</sub> values. The linear relationship between LaBO<sub>3</sub> surface ORR energetics and O *p*-band center can be understood based on a rigid band model, in which the energetics are related to electron interchange between the oxygen *p*-band and the Fermi energy level of the system. It is noted that the barrier of charge transfer between solids and O<sub>2</sub> molecules is not included in our energetic investigation due to the complexity of the calculations. Nonetheless, the existence of the linear relationship between O *p*-band center and the investigated LaBO<sub>3</sub> ORR energetics suggests the O *p*-band center, or equivalently, the O surface binding energy, could be a valuable descriptor for ORR activity.

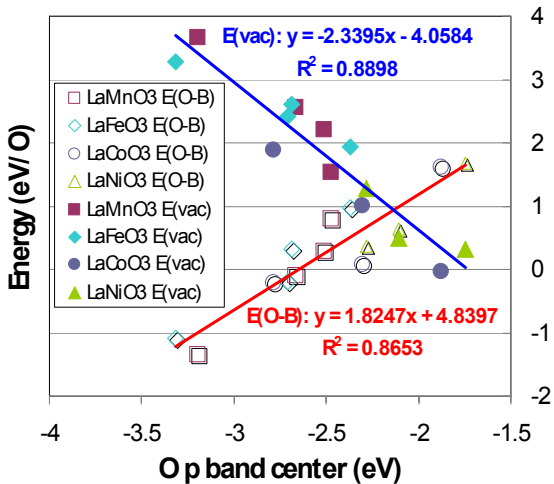


Figure 1: LaBO<sub>3</sub> (001) BO<sub>2</sub> surface oxygen vacancy formation and O-B adsorption energies for various B cation and U<sub>eff</sub>'s vs. O *p*-band center.

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